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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

Dynamics of *Green* AuNP formation and their application in core-shell nanostructures

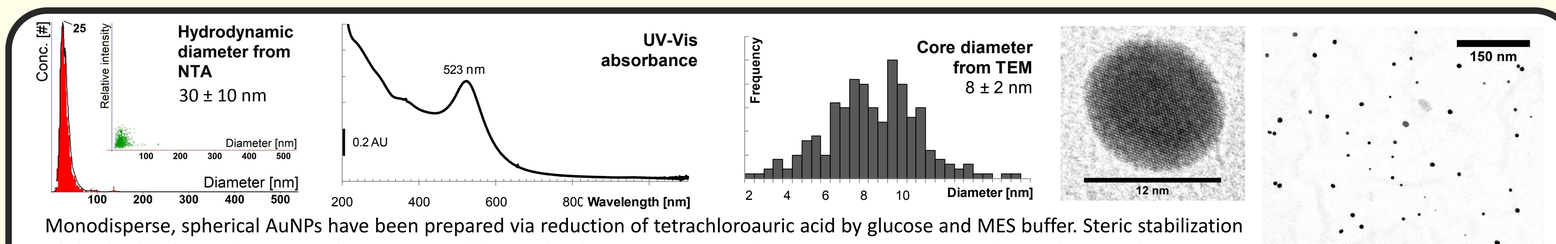
Christian Engelbrekt, Jingdong Zhang, Palle S. Jensen and Jens Ulstrup

DTU Chemistry, NanoDTU, Technical University of Denmark
DK-2800 Kgs. Lyngby, Denmark; contact: c-e@sol.dk

The formation of gold nanoparticles in our optimized synthesis is achieved through reduction of tetrachloroauric acid in 2-(N-morpholino)ethanesulphonic acid (MES) buffered glucose and stabilization by starch at room temperature. The formation has been followed by measuring the electrochemical potential, conductivity, pH, turbidity, UV-Vis extinction, core size and hydrodynamic diameter.

The synthesized AuNPs have been employed as core particles in advanced core-shell structures with highly porous platinum nanoparticle coating or copper oxide shells. These hold potentials as effective catalysts in fuel cells and methanol reformers.

GOLD NANOPARTICLES (AuNPs)

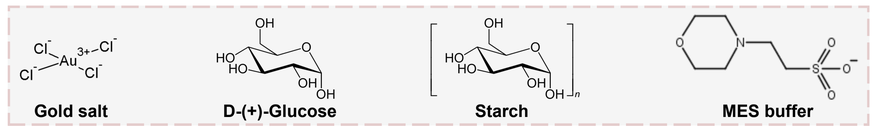


Monodisperse, spherical AuNPs have been prepared via reduction of tetrachloroauric acid by glucose and MES buffer. Steric stabilization of the freshly formed nanoparticles is increased by starch. The reaction proceeds at room temperature and completes in about 5 min. The nanoparticles have a gold core of 8 ± 2 nm, a Plasmon resonance peak at 523 nm and a hydrodynamic diameter around 30 nm.

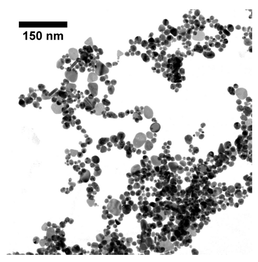
The AuNPs are very stable and no significant change is observed even after several years of storage at room temperature.

IN SITU MONITORING OF GOLD NANOPARTICLE FORMATION

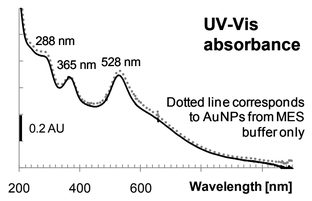
Every player has a different role



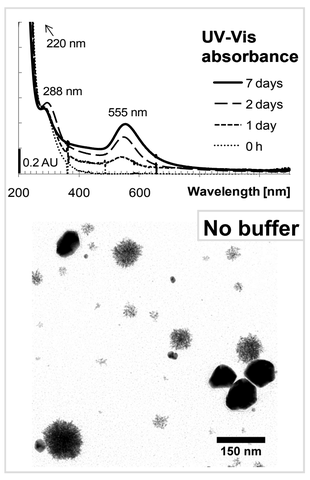
Glucose and Starch



Without glucose present the chemical reaction only changes slightly. The product on the other hand is different. The size increases and show a broader distribution. The AuNPs formed without starch to provide stabilization are considerably larger (6 - 40 nm, left). Besides spherical NPs also rods and sheets are common. The unstabilized particles tend to cluster more and arrange in long chains. The absorbance is significantly different from the standard AuNPs with two pronounced peaks around 288 nm and at 365 nm (right) and a broad shoulder on the plasmon band.



MES and other buffers

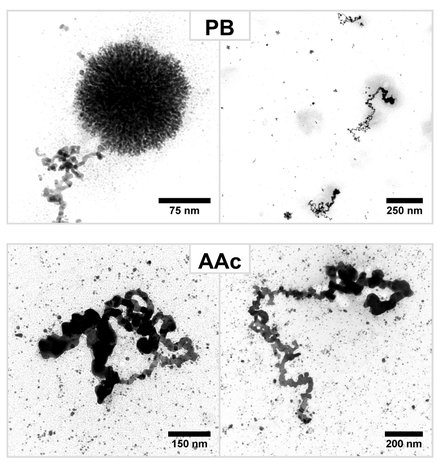


Synthesis of AuNPs without MES buffer is possible but very slow. The product is a mixture of very large NPs and dentritic clusters. Both in sizes up to more than 100 nm.

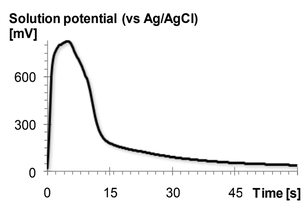
Phosphate (PB) and ammonia acetate (AAc) buffers were tested to provide buffer capacity without the oxidizing ability of MES. In both cases the reaction was very slow.

Particles with a very weak plasmon band at 560 nm and a hydrodynamic diameter of 100 ± 30 nm appeared in the PB sample. TEM showed dendritic structures similar to the no buffer case and highly sintered strings.

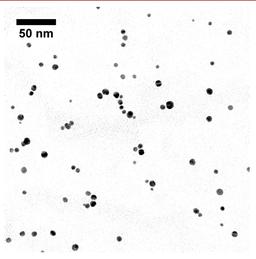
The AAc sample slowly turned brown and eventually a light brown precipitate settled leaving a colourless solution. TEM revealed non-uniform spherical NPs and also sintered strings.



Increased reaction temperature



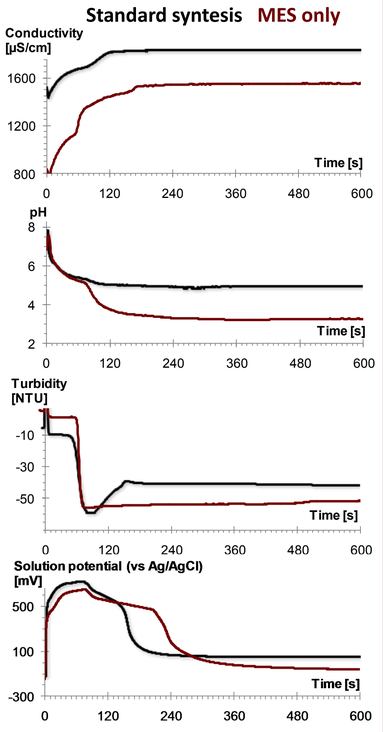
Temperature has a great influence on synthesis. Heating the solution to 60 °C increases the rate of reaction significantly and the synthesis completes in less than 20 s in contrast to 5 min at room temperature. The heated synthesis gives smaller particles below the detection limit of the NanoSight LM10. The rapid NP formation possibly results in a less sufficient coating of the NPs and chainlike arrangements.



MES is the main player

The MES buffer plays a very important role. Besides providing buffer capacity it also acts as the main reducing agent:

The first 60-80 s are believed to cover the reduction process which is (mostly) unaffected by the presence of starch and glucose. However, the remaining part of the NP formation is significantly different as observed in all parameters. This is proposed to relate to a widely different particle growth and nature of the product.

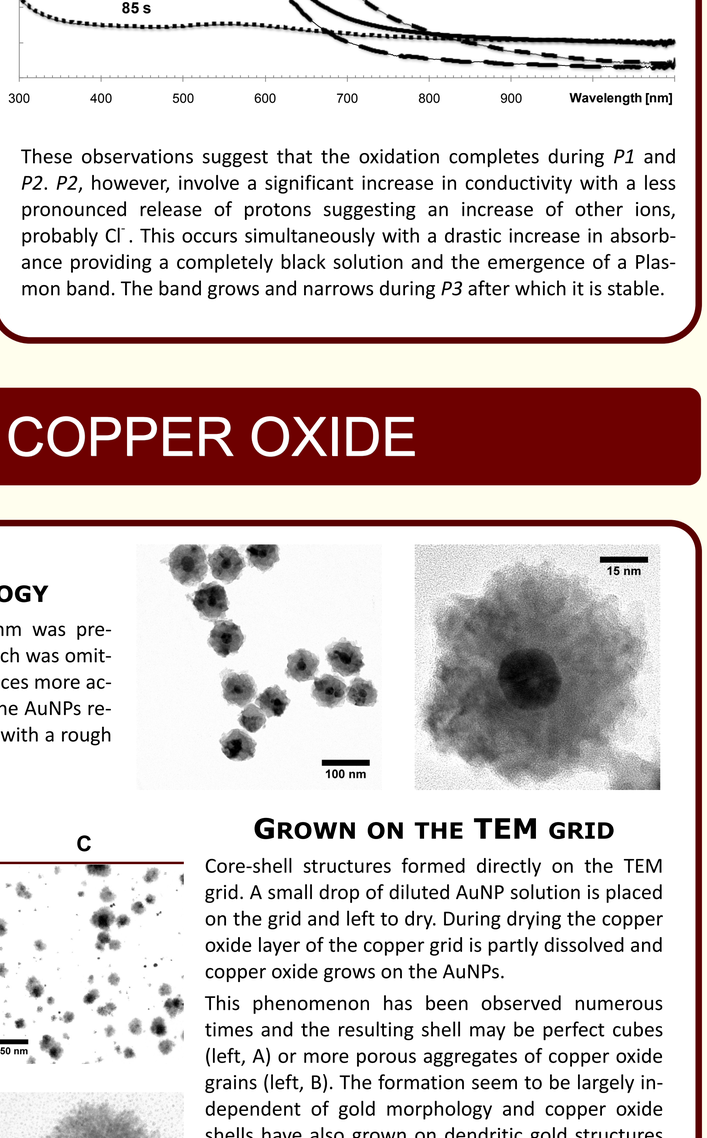


Viewing the synthesis from many angles

pH measurements reveals that almost even amounts of protons are released in *P1* and *P2* followed by 20 % during *P3*. An symmetrical increase/decrease is observed in the first 2 min of *P4*.

Conductivity showed an increase corresponding to 60 % of the total increase during *P1*, half of that during *P2* and only a slight increase in *P3*.

The **turbidity** measurements showed no change in extinction until going into *P2*. At this point the turbidity drops suddenly most likely due to a drastic increases in absorbance. *P3* initiates with a sudden recovery of turbidity until *P4* where turbidity stabilizes.



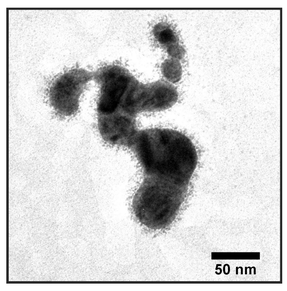
These observations suggest that the oxidation completes during *P1* and *P2*. *P2*, however, involve a significant increase in conductivity with a less pronounced release of protons suggesting an increase of other ions, probably Cl^-. This occurs simultaneously with a drastic increase in absorbance providing a completely black solution and the emergence of a Plasmon band. The band grows and narrows during *P3* after which it is stable.

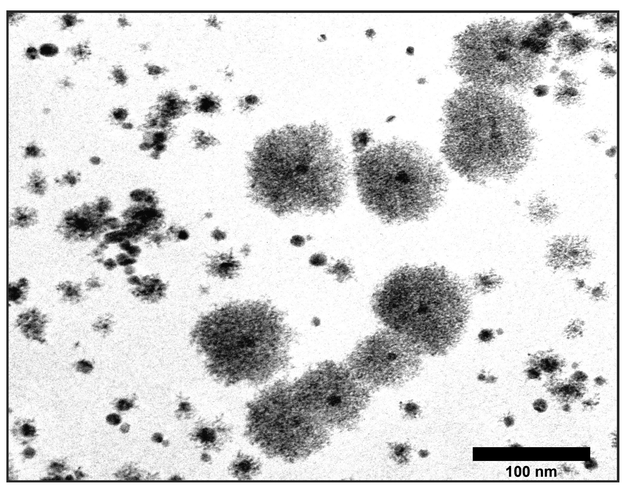
GOLD / PLATINUM

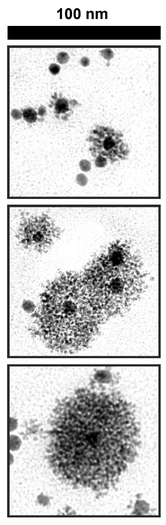
AuNP cores with a PtNP coating

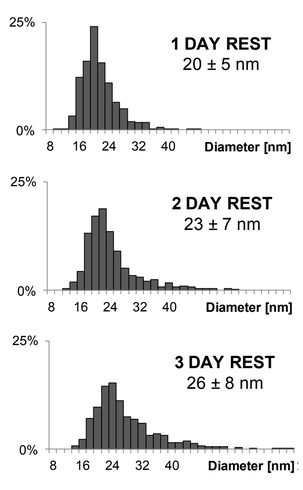
The freshly formed AuNPs can be used without any pre-treatment to prepare bi-metallic nanostructures consisting of a single AuNP core covered with a fine matrix of individual PtNPs around 2 nm (below). The AuNP solution is allowed to *rest* (no heating/stirring) to accommodate aggregation of glucose, MES and starch around the AuNPs. The growing coating layer serves as a scaffold. Subsequently added platinum ions diffuse into the coating and are reduced to form trapped NPs. The resting time governs the thickness of the coating and the size of the core/shell structure (below, right).

The procedure can be applied to other core structures from our recipe, such as sintered AuNP clusters, to give a series of Au/Pt core/shell structures (right).







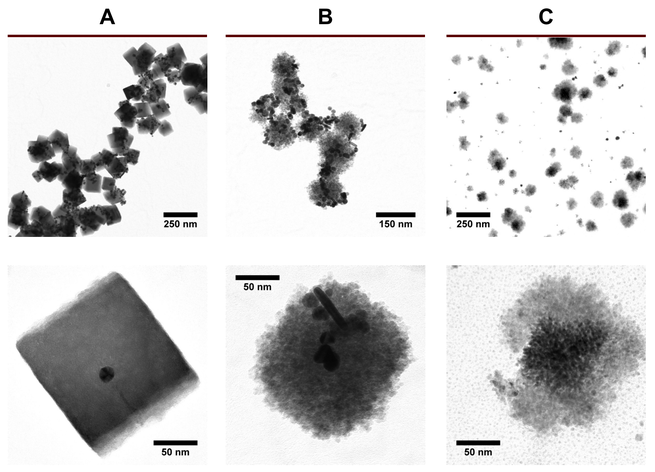


GOLD / COPPER OXIDE

Rough surface morphology

Uniform spherical nanostructures below 100 nm was prepared with AuNPs from the standard recipe. Starch was omitted in the AuNP synthesis to make the gold surfaces more accessible. $CuCl_2$ was reduced in the presence of the AuNPs resulting in gold-copper oxide core-shell structure with a rough surface morphology (right).

Grown on the TEM grid



Core-shell structures formed directly on the TEM grid. A small drop of diluted AuNP solution is placed on the grid and left to dry. During drying the copper oxide layer of the copper grid is partly dissolved and copper oxide grows on the AuNPs.

This phenomenon has been observed numerous times and the resulting shell may be perfect cubes (left, A) or more porous aggregates of copper oxide grains (left, B). The formation seem to be largely independent of gold morphology and copper oxide shells have also grown on dendritic gold structures (left, C).

The presence of core shell structures with copper from the TEM grid is very area specific which may be related to the drying process.

The details of the mechanism behind this is currently under investigation.